5/9/86

FILE COPY

Shaughnessy No.:116001

Date Out of EAB: MAY 09 1986

To: Robert Taylor
Product Manager 25
Registration Division (TS-767)

From: Samuel M. Creeger, Chief
Review Section #1
Exposure Assessment Branch
Hazard Evaluation Division (TS-769)

Attached, please find the EAB review of...

Reg./File # : 464-EUP-IT

Chemical Name: Triclopyr

Type Product : Herbicide

Product Name : GARLON ~~3A~~ 4

Company Name : DOW

Purpose : EUP in aquatic sites

Date Received: 11/8/85

Action Code(s): 750

Date Completed: MAY 09 1986

EAB #(s) : 6083

Days: 7

Deferrals to:

____ Ecological Effects Branch

____ Residue Chemistry Branch

____ Toxicology Branch

Monitoring study requested by EAB: ☐

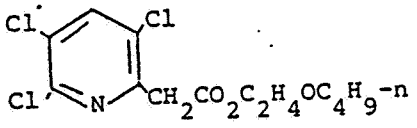
Monitering study voluntarily conducted by registrant: ☐

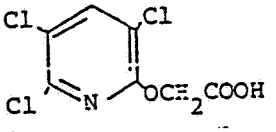
1.a CHEMICAL:

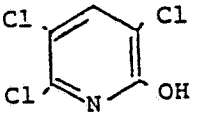
TRICLOPYR,

3,5,6-Trichloro-2-pyridinyloxyacetic acid, butoxy ethyl ester.

GARLON 3A







1.b Physical Properties:

Not included with this submission-see EAB review of May 13, 1980. Note Octanol/Water partition coefficient of 1.23×10^4.

2. TEST MATERIAL:

2,6-^{14}C-pyridine-radiolabeled triclopyr and triclopyr butyl ester

3. STUDY/ACTION TYPE:

An Experimental Use Permit for the Control of Woody Plants and Broad Leaf on Streams, Canals and Ditch Banks and in Ponds, Lakes, Marshes and Reservoirs.

4. STUDY IDENTIFICATION:

Photodegradation on Soil, Ref. No. 161-3.

Soil Dissipation, Ref. No. 164-2.

Anaerobic Soil, Ref. No. 164-1.

Forestry Field Dissipation, Ref. No. 164-3.

5. REVIEWED BY:

Akiva D. Abramovitch, Ph.D.
Chemist
Environmental Chemistry Review Section 1/EAB/HED/OPP

Abramovitch
MAY 09 1986
Date: / /85

6. APPROVED BY:

Samuel M. Creeger, Chief
Supervisory Chemist
Environmental Chemistry Review Section 1/EAB/HED/OPP

Samuel M Creeger
MAY 09 1986
Date: / /85

7. CONCLUSIONS:

Required data for this experimental use permit of Triclopyr as an aquatic herbicide and their status are as follows:

Data Requirement	Status
Hydrolysis	Satisfied (EAB review of 5/13/80).
Aqueous Photolysis	Satisfied (EAB review of 7/6/78).
Aerobic Aquatic Metabolism	Not satisfied.
Aerobic Soil Metabolism	Satisfied (EAB review of 7/6/78).
Accumulation in Fish	Not satisfied.
Leaching	Satisfied only for this EUP (EAB review of 7/6/78). An adsorption/desorption study will be needed for registration.
Irrigated Crop Data or a label statement.	Not satisfied.

Hydrolysis

The hydrolysis study was accepted by the EAB reviews of May 13, 1980 and July 6, 1978.

Reported Results:

Temerature (°C)	pH	Half Life (day) 5	7	9
25		84.0	8.7	0.3
15		208.8	25.5	1.7

Triclopyr, the major hydrolysis product of triclopyr butyl ester, did not undergo significant hydrolysis within a nine month period at pH's 5, 7.2 and 8.3 at 15, 25 and 35°C.

Fish Accumulation

The fish accumulation studies reported in the EAB review of 7/6/78 do not satisfy the current EAB data requirement. According to the EAB review of 7/6/78, one study was conducted in a flow through system with 1.1 ppb of trichloropyridinol but not the with the parent compound and the accumulation period lasted only six days (accumulation should last at least 28 days) without demonstrating that accumulation leveled off. In addition, the identity of the ^{14}C material accumulated in the fish was not determined. In view of the proposed use near and in water and the high octanol/water partition coefficient, fish accumulation data should be submitted before an EUP is granted.

Aqueous Photolysis

The aqueous photolysis study satisfied the EAB data requirement according to the EAB review of 7/6/78. Photodegradation in water appears to be a major environmental dissipation pathway. The parent triclopyr undergoes

fast degradation under natural sunlight conditions with a half life of less than 24 hours. The first photodegradation product is 3,5,6-trichloro-2-pyridinol which in turn is photodegraded at a faster rate than the parent compound.

Photolysis on Soil

As noted in section 10.1, below, the photolysis on soil study did satisfy the EAB data requirement for registration.

Aerobic Soil Metabolism

The study satisfied the EAB data requirement according to an EAB review of 7/6/78. When the aerobic soil degradation of triclopyr was studied, the parent compound degraded to trichloro-2-pyridinol first, then to trichloromethoxypyridine and eventually to carbon dioxide, with 7-30% evolution of $^{14}CO_2$ within 375 days. The degradation half life of the parent compound was 79-156 days at 15°C (see EAB review of 7/6/78 for the characteristics of the soil) and the major degradate was 3,5,6-trichloro-2-pyridinol (accounting for about 60% of the initial ^{14}C).

Anaerobic Soil

The anaerobic soil metabolism data requirement is satisfied by the current submission. The data indicates that triclopyr and its degradates will persist in the soil much longer under anaerobic conditions than under aerobic conditions (half life of 3.5 years under anaerobic conditions).

Leaching

The study satisfied the EAB data requirement according to the EAB review of 7/6/78. Triclopyr is a leachable compound. Its degradate, trichloropyridinol, has a lesser leaching potential than triclopyr.

Field Dissipation

The data included and reviewed in this submission indicates that the triclopyr will dissipate on the ground and in forest ecosystem with a half life of 20 days. Further information is needed about the dissipation of 3,5,6-trichloro-2-pyridinol and since the study was conducted only to a depth of 6" and since triclopyr is a leachable compound, it is not clear whether dissipation was due to degradation or leaching. For the purpose of registration on terrestrial sites, this data requirement is not satisfied.

8. RECOMMENDATIONS:

For this EUP, the following data gaps exist and need to be filled:

- 0 Fish accumulation.
- 0 Aerobic aquatic metabolism.
- 0 Irrigated crop data or a statement on the label restricting use of treated water for irrigating food or feed crops.

9. BACKGROUND:

A. Introduction:

Previous studies on Triclopyr, the active ingredient in GARLON 3A herbicide, were reviewed with regard to its use in GARLON 3A and GARLON 4A for the control of woody plants and broad leaf weeds on rights-of-way, forests and industrial sites. Currently, DOW is seeking an experimental use permit to ship and use GARLON 3A herbicide for the control of woody plants and broad leaf weeds on streams, canals and in lakes, ponds and reservoirs. This experimental use calls for the use of 12000 pounds of Triclopyr (the active ingredient) in 4000 gallons of GARLON 3A per year on 20 sites in a total of 8 states. No more than 40 acres per state will be treated per year. No more than 400 acres will be treated over a two year period. The application of GARLON 3A herbicide calls for spraying 1/3-1 1/2 gallons of the herbicide in 20-100 gallons of water. The water solubility of triclopyr is 430-440 ppm at 24.5°C.

B. Directions for Use:

See attached copy of supplemental labeling.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

10.1 A. Study Identification: Photodecomposition of Triclopyr Butoxy Ethyl Ester on Soil Surfaces.

The study was conducted by R. L. Swann and S. M. Unger of the Residue/Environmental/Metabolism Research, Agricultural Products Department of Dow Chemical.

B. Materials and Methods:

A sandy loam soil fortified at 1 ppm with a ^{14}C labeled triclopyr butoxy ethyl ester (labeled at the 2,6-positions of the pyridine ring) was irradiated for 28 days under a sunlamp (information about the intensity and range of the irradiating light was not submitted with the report).

C. Reported Results:

After 28 days of continuous irradiation, 83% of the butoxy ethyl ester of triclorpyr ester was hydrolyzed to the acid in both irradiated and non-irradiated samples. The irradiated samples, showed an additional 7% of the butoxy ethyl ester being converted to 3,5,6-trichloro-2-pyridinol.

D. Study Author's Conclusions:

The study author concluded that triclopyr is only slightly susceptible to soil surface photolysis. Hydrolysis and photolysis products found in this study were identical to ones observed in the aerobic soil degradation studies conducted previously (see EAB review of 7/6/78 for review of the mentioned two references by H. D. Bidlack and coworkers).

E. Reviewer's Discussions and Interpretations of Study Results:

The study results could not be validated since the range and intensity of the irradiating light were not specified and it is not clear whether natural sunlight conditions were simulated. An aqueous photolysis study was conducted under natural sunlight (EAB review of 7/6/78) and fast degradation was reported with a half life of less than 24 hours (2 hours of midday California sun) with the formation of trichloropyridinol. The latter compound underwent even a faster degradation than the parent compound to pyridine polyols that degraded further to form carbon dioxide (J. W. Hamaker, Dow report no. GS-1467 reviewed in EAB report of 7/6/78). On the other hand, this photolysis study on soil indicates that photolytic degradation on soil is not a major degradation pathway.

10.2A Study Identification: Anaerobic Degradation of Triclopyr Butoxyethyl Ester.

The study was conducted by D. A. Laskowski and H. D. Bidlack of the Residue/Environmental/Metabolism Research, Agricultural Products Department of Dow Chemical.

B. Materials and Methods:

Cecil and Norfolk soil samples were collected from the top 6" of soil profiles located in Georgia and Virginia (see attachment for soil analysis). The soils were amended with ground alfalfa and enough water to provide a water layer 2 cm over the soil and were incubated in darkness under nitrogen for 30 days at 25°C before treated with the radiolabeled butoxy ethyl ester of triclopyr (see section 2). Absence of carbon dioxide formation (a trap of aqueous NaOH was used) indicated that anaerobic conditions were achieved. The soil was fortified with the radiolabeled test chemical to 1 ppm on an oven-dry soil weight basis and the system was purged with nitrogen and maintained under nitrogen throughout the experiment. Samples were taken at specified time intervals (0, 1, 7, 14, 20, 60, 100, 201 and 365 days) and analyzed. Water used to ensure anaerobic conditions was separated from the soil and analyzed separately. The amount of ^{14}C material in the water and in the $^{14}CO_2$ trap was quantitated by LSC. Soil samples (10 gm) were extracted with methyl tertiary butyl ether (MTBE) in the presence of 10 ml of 1.5 M phosphoric acid and the radioactivity content in each phase was quantitated by LSC. The identity of the radioactive extracts in the MTBE was determined by HPLC and GC/MS in reference to authentic samples. Soil samples were combusted and the generated $^{14}CO_2$ was counted by LSC to determine the total and unextracted soil residues. In order to validate the analytical methods and to assure that no decomposition occurred during the extraction and the analysis, spiked soil and water samples were also extracted and analyzed with good recoveries and no noticeable decomposition (hydrolysis) occurred during the workup.

C. Reported Results:

The ester (parent compound) hydrolyzed within one day to triclopyr which was then converted slowly to 3,5,6-trichloro-2-pyridinol (20-25% formed in 365 days) as the only noticeable degradion product. The estimated half lives were 1300 days in both the Norfolk and the Cecil sandy loam soils (see attached graphs).

D. Study Author's Conclusions:

The author concluded that decomposition of triclopyr occurs under both aerobic and anaerobic conditions to identical products (carbon dioxide, 3,5,6-trichloro-2-pyridinol and 3,5,6-trichloro-2-methoxypyridine), but the breakdown rate was much slower in absence of oxygen.

E. Reviewer's Discussions and Interpretation of Study Results:

The study appeared to be conducted carefully and to provide valid scientific results and the reviewer did not find a cause to question the results or disagree with the author's stated conclusions. The reviewer would like to emphasize that the data indicates that triclopyr residues are likely to persist in soil for a long time under anaerobic conditions (half lives of 3.5 years).

10.3 A. Study Identification: Soil Dissipation, Residues of Triclopyr in Soil When Applied by Ground to Right-of-Way.
The study was conducted by D. E. M. Plaumann, M. M. Mackasey and P. Oostenbrink of the Agricultural Research and Development, DOW Chemical Canada Inc., in Ontario, Canada.

B. Material and Methods:

GARLON 4 was applied via ground equipment to a power line right-of way at the rate of 3.84 kg a.i./ha. Soil samples were randomly collected from the 0-6" depth and a 500 gm sample of vegetation was also collected before spraying, immediately after the spray dried off and at 1, 3, 7, 14, 28, 56 and 274 days after application. Samples were heated with methanolic sodium hydroxide, shaken and the solvent decanted. Then, an aliquot was taken, diluted with water, acidified, saturated with salt and partitioned into diethyl ether. The ether fractions were combined and partitioned with aqueous sodium bicarbonate solution. The sodium bicarbonate fraction was then acidified and extracted twice with ether. The ether fractions were combined, concentrated and an aliquot was reacted with diazomethane to obtain the methyl ester of triclopyr for GLC analysis (EC detector). Recoveries obtained by the method were tested with spiked authentic samples and were found to average 85% for soil samples and 71% for the forest litter while the lower limits of quantitation for the method was 0.1 ppm for the triclopyr (acid). For 3,5,6-trichloro-2-pyridinol the lower quantitation limits of the method was 0.05 ppm and recoveries averaged 77% in the soil.

C. Reported Results:

Averaged residues immediately after spraying were 6.2 ppm and the vegetation had average residues of 257 ppm (192-294 ppm). Within 56 days, residues in the soil and vegetation fell to 0.75 and 4.4 ppm, respectively. Half life estimations for triclopyr (from the attached data) were 20 and 5 days in the soil and vegetation, respectively.

D. Study Author's Conclusions:

The author noted that soil residue values did not follow the expected pattern when values dropped initially very rapidly and then rose again sharply. The author postulated that the observed pattern was probably due to the incorporation of extraneous plant material (containing higher residues than the soil) into the soil samples.

E. Reviewer's Discussion and Interpretation of Study Results:

The study should have been conducted to greater depths than 6" since triclopyr is a leachable compound. The dissipation of the major degradate, 3,5,6-trichloro-2-pyridinol, should have also been determined under the study conditions. Weather (including rainfall data) conditions should have been reported. This study is not an acceptable field dissipation study.

10.4 A. Study Identification: Residues of Triclopyr in Soil When Aerially Applied to a Forest Ecosystem.

The study was conducted by D. E. M. Plaumann, M. M. Mackasey and P. Oostenbrink of the Agricultural Research and Development, DOW Chemical Canada Inc., in Ontario, Canada.

B. Material and Methods:

GARLON 4 was applied aerially at a rate of 3 kg a.i./ha to an 8 ha. site. Three plots were uncovered by trees and brush and free from forest litter. Three plots were uncovered by trees and brush but did have forest litter. From each plot, ten 1" core samples from 0-6" were combined and identified as the composite soil sample from that particular plot on that particular date. Sample collection was done on the day before treatment, immediately after treatment and on days 1, 3, 7, 14, 28, 56 and 251 after treatment to establish a residue degradation curve. Analysis was performed for triclopyr and for 3,5,6 trichloro-2-pyridinol. For analysis samples were heated with methanolic sodium hydroxide, the supernatant solution was decanted and the volume was calibrated so that aliquots can be taken. An aliquot was then taken, diluted with water, acidified and extracted with diethyl ether. The ether fractions were combined and extracted with aqueous sodium bicarbonate. The sodium bicarbonate was then acidified and extracted with ether. The combined ether extracts were then concentrated and treated with diazomethane to obtain the methyl ester of triclopyr for the purpose of chromatographic analysis by GLC with an EC detector. The lower quantitation limit for the method is 0.1 ppm and recoveries for triclopyr averaged 85% for the soil and 71% for the litter. For analysis for 3,5,6-trichloro-2-pyridinol extractions

were done with benzene (instead of diethyl ether) and the benzene extract was treated with N,O-bis (trimethylsilyl) acetamide to form 2,3,5-trichloro-6-(trimethylsiloxy) pyridine which was then quantitated by GLC (EC detector). The lower limit of quantitation for the method is 0.05 ppm. Recoveries were checked by analyzing untreated controls spiked with known levels of pyridinol and averaged 77% in soil.

C. Reported Results:

The concentration of triclopyr in the soil was the highest a day after application (averaged 3.7 ppm, 2.5-5.2 ppm) and dropped to one tenth of its original value within 58 days (averaged 0.33 ppm, highest value obtained 0.56 ppm). In the litter covered soil the residues of triclopyr were considerably less throughout the study and ranged from the initial average value of 3.0 ppm to 0.03 ppm after 58 days. Residues in the litter ranged from an initial averaged value of 0.45 ppm to a value of 0.18 ppm 58 days after application. Difficulties were encountered in obtaining meaningful analytical results for the 3,5,6-trichloro-2-pyridinol.

D. Study Author's Conclusions:

The rate of disappearance of triclopyr is very rapid in soil and the little triclopyr found in the litter is virtually gone within 58 days. In both cases, the half life is between 10 and 20 days in both bare and litter covered soils.

E. Reviewer's Discussion and Interpretation of Study Results.

The study should have been conducted to greater depths than 6" since triclopyr is a leachable compound residues and were found at the 6" depth. The dissipation of the major degradate, 3,5,6-trichloro-2-pyridinol, should have also been determined under the study conditions. Weather (including rainfall data) conditions should have been reported. It is not clear to the reviewer why difficulties were encountered in the analysis of the trichloro-2-pyridinol when good recoveries were reported with spiked authentic samples. This study does not satisfy the requirements.

11. COMPLETION OF ONE LINER

No data included.

12. CBI APPENDIX

Attachment.